

# Electron doping and magnetic moment formation in N- and C-doped MgO

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## Abstract

The formation of the magnetic moment in C- and N-doped MgO is the result of a delicate interplay between Hund's coupling, hybridization and Jahn-Teller distortion. The balance depends on a number of environmental variables including electron doping. We investigate such a dependence by self-interaction corrected density functional theory and we find that the moment formation is robust with respect to electron doping. In contrast, the local symmetry around the dopant is more fragile and different geometries can be stabilized. Crucially the magnetic moment is always extremely localized, making any carrier mediated picture of magnetism in  $d^0$  magnets unlikely.

In the last few years an intensive research effort has been devoted to synthesize diluted magnetic semiconductors (DMS) in the hope of finding a material with semiconducting properties and ferromagnetism at room temperature (RT). Standard DMS are produced by doping conventional semiconductors with transition metals [1], and the magnetic coupling usually originates from some carrier-induced mechanism. More recently two main experimental facts have challenged this “traditional” picture. Firstly magnetism was claimed in oxides DMS on both sides of the metal insulator transition [2], indicating that carriers alone are not sufficient to explain the magnetism and that intrinsic defects play a crucial rôle [3]. Secondly, defect-rich or intentionally  $p$ -doped oxides revealed the possible evidence for RT magnetism. This second class of phenomena has been named  $d^0$  magnetism, indicating that no ions with partially filled  $d$ -shells are at the origin of

the magnetic moment. The examples of  $d^0$  magnets are many and include thin films of  $\text{HfO}_2$ [4],  $\text{TiO}_2$ [5, 6, 7],  $\text{In}_2\text{O}_3$ [8], C-doped  $\text{ZnO}$ [9, 10], and nanoparticles of different materials[11]. Furthermore studies over chemically synthesized powders suggest that  $d^0$  magnetism can be found in bulk materials and not only in surfaces[12, 13].

Usually the formation of the magnetic moment is explained in terms of spin-polarized holes localized either at cation vacancies molecular orbitals [14, 15] or at the  $p$ -orbitals of the doping impurity[15, 16, 17, 18]. However, a clear understanding of the driving mechanism behind  $d^0$  ferromagnetism is still unavailable. In order to understand its uniqueness we recall that the record Curie temperature ( $T_C$ ) for GaAs:Mn (the DMS prototype) is 200 K[19], obtained for 8 % Mn doping and the largest hole concentration achievable. Since cation vacancies in oxides hardly reach concentrations exceeding 1 % and both C and N cannot be doped abundantly [10], one can conclude that a similar  $T_C$  in  $d^0$  magnets would require a magnetic interaction around 10 times stronger than that between Mn in GaAs:Mn. Considering that our argument neglects any considerations about percolation and the fact that even the origin of the magnetic moment is not established with certainty, it is fair to say that any claim of  $d^0$  ferromagnetism should be considered exceptional.

In this arena almost all the theoretical predictions are based on density functional theory (DFT) using either the local spin density (LSDA) or the generalized gradient approximation (GGA). These describe the ground state of  $d^0$  magnets as ferromagnetic and metallic, and in fact most of the time as half metallic. However strong electron correlations may play a fundamental rôle in the magnetic moment formation, which subtly depends on the interplay between covalency, Hund's coupling and polaronic distortion around the impurity [15]. Corrections to the LSDA/GGA such as the LDA+ $U$  or the self-interaction correction (SIC) schemes often return an insulating ground state and no long range magnetism. For instance in rock-salt oxides ( $\text{MgO}$ ,  $\text{CaO}$  and  $\text{SrO}$ ) doped with

N substituting for O [15, 17, 18], one finds that the extra hole entirely localizes around one of the  $2p$  orbitals as a consequence of the coupling with phononic modes. Thus the physics of these materials reminds that of the manganites [20], with the difference that in  $d^0$  magnets the moment is associated to the  $2p$  atomic shell.

In analogy with the manganites, one expects that the interplay between charge, spin and orbital degrees of freedom may lead to a number of cooperative physical phenomena[20]. In particular the long range magnetic order in  $d^0$  magnets is intimately related to the formation of the moment itself [16], with Stoner and spin-wave excitations probably competing. Thus both the moment and the magnetic coupling becomes sensitive to environmental variables such as doping, charge fluctuations and temperature. In this work we investigate the effects of one of these variables, namely electron doping, over the magnetic moment formation in C- and N-doped MgO. In particular we will answer two fundamental questions: 1) does the magnetic moment survive to electron doping? and 2) what is the response of the lattice to such an electron doping?

Our calculations are performed by using a development version of the DFT code SIESTA[21], implementing the atomic SIC scheme (ASIC)[22]. The core electrons are treated with norm-conserving Troullier-Martin pseudopotentials and the valence charge density is expanded over a numerical orbital basis set, including double- $\zeta$  and polarized functions [21]. The real space grid has an equivalent cutoff larger than 800 Ry. Calculations are performed with supercells of 96 atoms including  $k$ -point sampling over at least 25 points in the Brillouin zone. Atomic coordinates are relaxed by conjugate gradient until the forces are smaller than 0.01 eV/Å.

As already mentioned when N or C replace O ( $N_O$  and  $C_O$ ) the MgO local cubic symmetry is reduced[15]. In both cases the bonds with Mg are longer than the Mg-O one as a consequence of the different ionic radii. However, for  $N_O$  two of the three  $p$ -bonds

contract and the hole localizes around the remaining long one ( $N_O$  configuration), while for  $C_O$  only one bond contracts and the two holes localize around the remaining two long bonds ( $C_O$  configuration). In both cases the system is insulating with either one ( $C_O$ ) or two ( $N_O$ ) fully filled  $p$  orbitals. We now consider  $C_O$  and add a fractional charge  $\Delta n$  to the supercell, with charge neutrality ensured by a compensating positive background. One then expects that the electronic structure and the relaxation becomes progressively similar to that of  $N_O$ .

Our results are presented in Tab. I, where we list the Mg-C bond lengths,  $d_{\text{Mg-C}}$ , and the cell magnetic moment,  $\mu$ , as a function of  $\Delta n$ . Importantly all the structural calcu-

$\Delta n$ ( $-e$ )	$d_{\text{Mg-C}}$ ( $\text{\AA}$ ) [ $C_O$ -Rel]	$d_{\text{Mg-C}}$ ( $\text{\AA}$ ) [ $N_O$ -Rel]	$\mu$ ( $\mu_B$ )
0.0	2.176 (4), 2.152 (2)	2.176 (4), 2.152 (2)	2.0
0.2	2.163 (4), 2.146 (2)	2.170 (2), 2.161 (2), 2.143 (2)	1.8
0.4	2.149 (4), 2.136 (2)	2.157 (2), 2.143 (2), 2.131 (2)	1.6
0.6	2.135 (4), 2.120 (2)	2.141 (2), 2.126 (2), 2.120 (2)	1.4
0.8	2.120 (4), 2.110 (2)	2.122 (2), 2.116 (2), 2.112 (2)	1.2
1.0	2.105 (4), 2.099 (2)	2.105 (2), 2.099 (4)	1.0

Table I: Mg-C bond length,  $d_{\text{Mg-C}}$ , and supercell magnetic moment  $\mu$ , of  $C_O$  as a function of the electron doping  $\Delta n$ . We indicate as [ $C_O$ -Rel] the relaxed structure obtained from an atomic relaxation initiated at the  $\Delta n=0$   $C_O$  geometry, and as [ $N_O$ -Rel] that initiated at the  $\Delta n=0$   $N_O$  geometry. In the bracket beside the bond length we indicate the degeneracy of the particular bond.

lations turned out to be sensibly dependent on the initial conditions for the relaxation. In particular we find that all the relaxations initialized at the  $\Delta n=0$   $C_O$  configuration converged to a local geometry presenting 4 long bonds and 2 short ones, i.e. still pre-

senting the symmetry of  $C_O$ . In contrast those initialized at the  $\Delta n=0$   $N_O$  configuration converged to a local geometry with two long, two short and two intermediate bonds.

The changes in the electronic structure as a function of electron doping are illustrated in the cartoon of Fig. 1 for the two obtained geometries. In both cases the additional charge remains localized at the dopant site and the magnetic moment varies as  $\mu = (2 - \Delta n)\mu_B$ . The main difference between the electronic structures of the two geometries originates from their different orbital occupation. For the  $C_O$ -relaxed structure the fractional charge progressively occupies the minority empty doublet associated to the four long bonds, spreading evenly among them [see Fig. 1(a)]. In contrast the  $p$ -orbitals of the  $N_O$ -relaxed structure form a set of closely spaced singlets. Hence the additional fractional charge occupies the first of the available empty singlets and localized further along the direction of the bond of intermediate length [see Fig. 1(b)]. These differences persist up to  $\Delta n=1$  where the  $C_O$ -relaxed structure is metallic, while the  $N_O$ -relaxed is insulating.

Unfortunately the ASIC functional, although constructs a valuable potential so that atomic relaxation can be carried out, does not provide accurate total energies. Therefore we cannot distinguish energetically between the two geometries found. We have performed additional ASIC total energy calculations at the un-relaxed  $C_O$  and  $N_O$  geometries, which seems to suggest a crossover between the two at a doping of  $\Delta n=0.5$ , however also these calculations are affected by an intrinsic lack of accuracy and therefore the result must be taken with caution.

Given this uncertainty we decided to take a look at the theory for the local vibronic coupling. For manganites the Jahn-Teller distortion is driven by the coupling of doubly degenerate  $d$ -shell  $e_g$  states to the only two normal modes having the same symmetry. In contrast the  $2p$  levels of the N in MgO form a set of degenerate  $t_{1u}$  levels, which

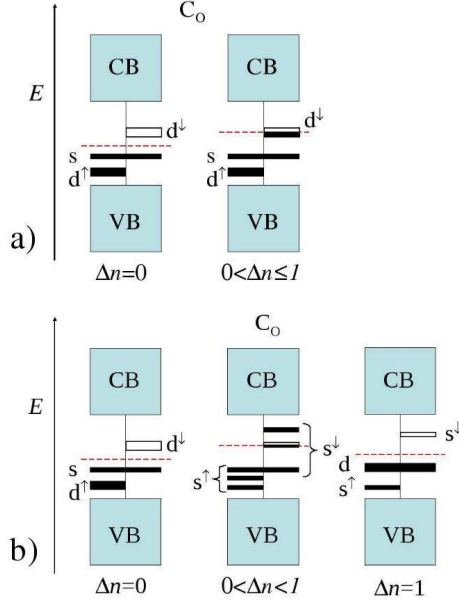


Figure 1: (Color on line) Cartoon representing the level occupation of  $C_O$  upon electron doping. In panel (a) the energy levels are those of the local geometry obtained from a relaxation initiated at the  $C_O$  configuration, while in (b) those obtained from a relaxation initiated at the  $N_O$  configuration. For  $\Delta n=0$ , in both cases a doubly occupied spin-polarized doublet ( $d^\uparrow$ ) is followed by a doubly occupied unpolarized singlet ( $s$ ) and separated by the Fermi level (red dashed line) from its minority spin component ( $d^\downarrow$ ). Upon doping ( $\Delta n > 0$ ), in (a) the minority doublet gets progressively filled, while in (b) the doublet further splits into two singlets and the additional fractional charge distributes over the lower of the empty minority singlets. In both cases the magnetic moment goes as  $\mu = (2 - \Delta n)\mu_B$ .

are coupled with normal modes of symmetry  $e_g$  and  $t_{2g}$ . Importantly, in this case the  $e_g$  modes tend to stabilize a tetragonal distortion, while the  $t_{2g}$  a trigonal one resulting in a competition between the two[23]. Furthermore, when anharmonic corrections are considered, a structure of  $C_2$  symmetry minimizes the energy. It is notable that the highest occupied level for one hole over the impurity in this geometry is  $1/\sqrt{2}(p_x \pm p_y)$  and could account for the orbital occupation found for the  $C_O$ -relaxed structure at  $\Delta n=1$ . Unfortunately, our relaxations always ends up with a tetragonal distortion and the symmetry around the impurity is never of  $C_2$ -type. The vibronic theory then predicts that

the ground state is the one with the hole localized on just one of the three  $p$  orbitals. Thus we conclude that simple symmetry arguments seem to support the relaxation initiated by the  $N_O$  atomic coordinates, i.e. the one converging to a local geometry having two long, two short and two intermediate bonds.

After having studied  $C_O$ , we briefly take a look at  $N_O$  under doping. This time we find that the unpaired singlet gradually fills upon electron doping, thus that the distortion gradually reduces to a perfectly cubic symmetry and the moment follows  $\mu = (1 - \Delta n)\mu_B$ . Interestingly we find that the residual hole always localizes over the longer of the Mg-N bonds and that no magnetic coupling is found for every  $\Delta n$ , despite the material remains metallic.

In conclusion, we investigated the effects of electron doping on the magnetic moment formation of N- and C-doped MgO. We find that for all doping concentrations the impurity levels are deep in the MgO gap and the magnetic moment is stable against charge fluctuations. However, lattice distortion always promotes the localization of the doping hole, thus reducing the chance of long range magnetic coupling between impurities.

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